Free Volume Effects on Rheological and Thermal Properties of Polymers and Polymer Blends

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SYNOPSIS

Using the free volume theory, general relations between viscometric and volumetric properties of polymers as functions of temperature and deformation conditions (shear rate or shear stress) have been derived. In particular, it has been shown that thermal expansion of polymers can be calculated from viscometric data. The obtained relations have been applied for description of the rheological behavior of polymer blends. Theoretical predictions have been compared with experimental data. Good agreement between theory and experiment has been stated if rheological properties of blends were compared at a constant shear rate.

INTRODUCTION

The concept of the free volume considered as an empty space between molecules resulting from their thermal motions and steric effects can be very useful in explaining many phenomena and properties of various polymer systems in different physical states. This concept has been successfully used for explanation of temperature and pressure dependences of viscosity,[1] the plasticization mechanism,[2] the effect of molecular weight[3] and of a gas addition[4] on viscosity, etc.

In our previous paper,[5] an attempt was made to apply the free volume theory for prediction of rheological properties of molten polymer blends. This approach leads to the conclusion that the rheological behavior of blends of known composition at defined temperature and deformation conditions (shear rate or shear stress) can be characterized only if the viscosities, specific volumes, and thermal expansion coefficients of components and the specific volume of blend are determined.

This paper deals with some problems which arose from these studies. The most important of them are:

- Elimination of the thermal expansion coefficients due to the fact that both the thermal expansion and the temperature dependence of viscosity result from temperature changes of the free volume.
- Determination of the specific volume as a function of deformation conditions (shear rate or shear stress).
- Experimental verification of some previous assumptions related to the properties of polymer blends.

THEORETICAL

General Treatment

The free volume effect on viscosity of many polymer systems can be analytically described using the Doolittle equation[6]:

$$\ln \eta = C + B \frac{V_0}{V_f} \tag{1}$$

where V_0 = occupied volume, V_f = free volume, and B and C are material constants independent of temperature (B is approximately equal to unity[2]). Between the specific volume V and the quantities V_f and V_0 there exists the following relationship:

$$V = V_f + V_0 \tag{2}$$

Generally it can be assumed that both V_f and V_0 are linear functions of temperature T, i.e.,

$$\frac{\partial^2 V_f}{\partial T^2} = \frac{\partial^2 V_0}{\partial T^2} = 0 \tag{3}$$

The thermal expansion coefficient of any individual volume appearing in eq. (2) can be defined in the following way:

$$\kappa_i = \frac{1}{V_i} \frac{\partial V_i}{\partial T} = \frac{\partial \ln V_i}{\partial T} \tag{4}$$

For molten polymer systems it can be assumed that the thermal expansion of the occupied volume is much smaller than that of the free volume. This is due to the fact that the thermal motions of atoms responsible for the expansion of the occupied volume are small as compared to the motions of whole molecules being an origin of the expansion of the free volume. This statement can be formulated as follows:

$$\kappa_f \gg \kappa_0 \tag{5}$$

Differentiating both sides of eq. (1) with respect to temperature and taking into account expression (4), one obtains

$$\frac{\partial \ln \eta}{\partial T} = -B \frac{V_0}{V_f} (\kappa_f - \kappa_0) \tag{6}$$

Further differentiation of eq. (6) with the use of assumption (3) leads to

$$\frac{\partial^2 \ln \eta}{\partial T^2} = 2B \frac{V_0}{V_f} \kappa_f (\kappa_f - \kappa_0) \tag{7}$$

Substituting expression (6) into (7), one obtains

$$\kappa_f = -\frac{1}{2} \frac{\partial^2 \ln \eta}{\partial T^2} \bigg/ \frac{\partial \ln \eta}{\partial T} \tag{8}$$

The value of V_0/V_f can be calculated from eq. (6), neglecting κ_0 according to (5) and substituting for κ_f expression (8):

$$\frac{V_0}{V_f} = \frac{2}{B} \left[\frac{\partial \ln \eta}{\partial T} \right]^2 \bigg/ \frac{\partial^2 \ln \eta}{\partial T^2} = \Theta \tag{9}$$

Suitable values of free and occupied volumes can be calculated from eqs. (2) and (9):

$$V_f = \frac{V}{1 + \Theta} \tag{10}$$

$$V_0 = \frac{\Theta V}{1 + \Theta} \tag{11}$$

The thermal expansion coefficient of specific volume of melt, κ, can be obtained differentiating eq. (2) with respect to temperature and applying expressions (4), (6), and (8):

$$\kappa = \kappa_f + \frac{1}{B} \frac{\partial \ln \eta}{\partial T} \frac{1}{1 + \Theta} \tag{12}$$

On other hand, the differentiation of eq. (10) with the use of (4) gives

$$\kappa = \kappa_f + \frac{\partial \Theta}{\partial T} \frac{1}{1 + \Theta} \tag{13}$$

Since both sides of eqs. (12) and (13) should be equal, the following relationship holds:

$$\frac{1}{B} \frac{\partial \ln \eta}{\partial T} = \frac{\partial \Theta}{\partial T} \tag{14}$$

This nonlinear differential equation of third order can be easily solved to obtain the functional dependence of viscosity on temperature in the form

$$\ln \eta = K + \frac{A}{T + D} \tag{15}$$

where A, D, and K are the constants of integration. Subsituting expression (15) into (9), one obtains

$$\frac{V_0}{V_f} = \frac{1}{B} \frac{A}{T + D} = \Theta \tag{16}$$

From eqs. (1), (15), and (16), it follows that $K = C$, i.e., eqs. (1) and (15) describing viscosity in terms of the free volume variations or temperature variations are equivalent. Assuming $D = 0$ or $D = T_0$ in eq. (15), one obtains two useful forms corresponding to the Arrhenius and Fulcher–Tamman equations,[1] respectively.

The above analysis shows that many factors describing the properties of polymer systems can be calculated if the functional dependence of viscosity on temperature is known. In particular, from eqs.

(8), (9), and (12) it follows that the thermal expansion coefficient of melt, κ, calculated from viscometric data [eqs. (15) and (16)] takes the form

$$\frac{\partial \ln V}{\partial T} = -\frac{1}{B} \frac{\partial \ln \eta}{\partial T} \frac{1}{\Theta(1 + \Theta)} \quad (17)$$

Considering expression (17), eqs. (9)–(11) are equivalent with those derived in our previous work[5] except that the estimation of free and occupied volumes requires no additional, independent measurements of the thermal expansion coefficient, but only the measurements of specific volume V at a given temperature and deformation conditions (shear rate or shear stress).

Experimental determination of specific volume of melts is usually done at static conditions, i.e., in the absence of the shear stresses. The specific volume measurements for polymer systems subjected to the shear flow are theoretically possible but very difficult for practical performance with a suitable accuracy.

Theoretical calculation of the shear effect on specific volume can be done assuming that the occupied volume of a system V_0 is independent of shear rate or shear stress. Taking into account expression (11), one obtains the following relationship for calculation of the specific volume as a function of the shear rate or shear stress:

$$V = \frac{1 + \Theta}{1 + \Theta_s} \frac{\Theta_s}{\Theta} V_s \quad (18)$$

where Θ_s and V_s are the values of parameters Θ and V, respectively, determined at static conditions, i.e., practically in the Newtonian flow region. The values of Θ should be determined either at a constant shear rate or a constant shear stress.

Applications to Polymer Blends

The general relations derived above can be applied to polymer blends only if the rules of changes of the quantities defined by eq. (1) with varying blend composition are known. According to our previous paper,[5] one can assume that:

(a) The occupied volume of blend V_{0b} is an additive quantity, i.e.,

$$V_{0b} = \sum_{i=1}^{n} w_i V_{0i} \quad (19)$$

(b) The free volume of blend V_{fb} is a nonadditive quantity, i.e.,

$$V_{fb} = \sum_{i=1}^{n} w_i V_{fi} + F(w_i, w_i, w_n) \quad (20)$$

where the function F describes the nonadditivity of the free volume and can be calculated from equation:

$$F = V_b - \sum_{i=1}^{n} w_i V_i \quad (21)$$

(c) The material constant C (C_b) fulfils the following condition:

$$C_b = \sum_{i=1}^{n} w_i C_i \quad (22)$$

(d) The material constant B is independent of the blend composition.

In eqs. (19)–(22) the following symbols have been used: w_i = weight fraction of ith component: V_{0i} = occupied volume of ith component; V_{fi} = free volume of ith component; V_i = specific volume of ith component; V_b = specific volume of blend, and C_i = material constant of ith component.

Substituting eq. (11) into (19), one obtains

$$V_{0b} = \frac{\Theta_b}{1 + \Theta_b} V_b = \sum_{i=1}^{n} w_i \frac{\Theta_i}{1 + \Theta_i} V_i \quad (23)$$

According to (18), expression (23) should be independent of deformation conditions and can be applied for experimental verification of additivity of occupied volume.

The identity of material constants C and K in eqs. (1) and (15), respectively, which has been shown above, makes possible the experimental verification of expression (22). Substituting the K values for blend and pure components calculated from (15) and (18) into (22), one obtains

$$\ln \eta_b - B\Theta_b = \sum_{i=1}^{n} w_i (\ln \eta_i - B\Theta_i) \quad (24)$$

If the additivity of the material constant C for blends holds true, eq. (24) can be used for direct calculations of the viscosity of blends of known composition and properties of pure components. For this purpose the value of the parameter Θ_b in eq.

(24) should be replaced by a value which can be obtained from experiments independent of measurements on the blend viscosity as a function of temperature and deformation conditions.

In the general case, the parameter Θ_b should be assumed to be a function of temperature and deformation conditions (shear rate or shear stress). A method which makes possible the calculation of the value of Θ_b at any shear rate from experimental data obtained at some reference conditions (e.g., at very low shear rate in the Newtonian flow region) will be described below.

For this purpose expression (1) should be differentiated with respect to the shear rate $\dot{\gamma}$ at constant shear stress τ, taking into account that the occupied volume V_0 is independent of shear rate:

$$\left[\frac{\partial \ln \eta}{\partial \dot{\gamma}}\right]_\tau = \left[\frac{\partial C}{\partial \dot{\gamma}}\right]_\tau + V_0 \left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_\tau \qquad (25)$$

Differentiation of eq. (22) gives

$$\left[\frac{\partial C_b}{\partial \dot{\gamma}}\right]_\tau = \sum_{i=1}^{n} w_i \left[\frac{\partial C_i}{\partial \dot{\gamma}}\right]_\tau \qquad (26)$$

Since

$$\tau = \eta \dot{\gamma} \qquad (27)$$

the application of eq. (25) separately for blend and pure components and the use of (26) leads to the following result:

$$V_{0b}\left[\frac{\partial V_{fb}^{-1}}{\partial \dot{\gamma}}\right]_\tau = \sum_{i=1}^{n} w_i V_{0i}\left[\frac{\partial V_{fi}^{-1}}{\partial \dot{\gamma}}\right]_\tau \qquad (28)$$

The derivatives in eq. (28) are very difficult to interpret since they do not relate to constant temperature. To obtain a relationship between suitable derivatives at constant shear stress and constant temperature, the total differentials of η and V_f as functions of shear rate and temperature should be taken into account:

$$d\eta = \left[\frac{\partial \eta}{\partial T}\right]_{\dot{\gamma}} dT + \left[\frac{\partial \eta}{\partial \dot{\gamma}}\right]_T d\dot{\gamma} \qquad (29)$$

$$dV_f = \left[\frac{\partial V_f}{\partial T}\right]_{\dot{\gamma}} dT + \left[\frac{\partial V_f}{\partial \dot{\gamma}}\right]_T d\dot{\gamma} \qquad (30)$$

Dividing both sides of eqs. (29) and (30) by dT at constant τ and rearranging, one obtains

$$\left[\frac{\partial \ln \eta}{\partial T}\right]_{\dot{\gamma}} \bigg/ \left[\frac{\partial \ln \eta}{\partial T}\right]_\tau$$

$$= 1 - \left[\frac{\partial \ln \eta}{\partial \dot{\gamma}}\right]_T \bigg/ \left[\frac{\partial \ln \eta}{\partial \dot{\gamma}}\right]_\tau \qquad (31)$$

$$\left[\frac{\partial V_f^{-1}}{\partial T}\right]_{\dot{\gamma}} \bigg/ \left[\frac{\partial V_f^{-1}}{\partial T}\right]_\tau$$

$$= 1 - \left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_T \bigg/ \left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_\tau \qquad (32)$$

On the other hand, from eqs. (5) and (6) after some transformations, it follows that

$$\left[\frac{\partial \ln \eta}{\partial T}\right]_{\dot{\gamma}} \bigg/ \left[\frac{\partial \ln \eta}{\partial T}\right]_\tau = \left[\frac{\partial V_f^{-1}}{\partial T}\right]_{\dot{\gamma}} \bigg/ \left[\frac{\partial V_f^{-1}}{\partial T}\right]_\tau \qquad (33)$$

Considering expressions (27) and (31)–(33), one obtains the following end result:

$$\left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_\tau = -\left[\frac{\partial \ln \eta}{\partial \ln \dot{\gamma}}\right]_T^{-1}\left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_T \qquad (34)$$

In the region of the power law applicability, eq. (34) reads

$$\left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_\tau = \frac{1}{1-n}\left[\frac{\partial V_f^{-1}}{\partial \dot{\gamma}}\right]_T \qquad (35)$$

where n is the power law exponent. Substituting eq (35) into (28) and integrating (V_0 and n are independent of shear rate), one obtains

$$\frac{V_{0b}}{1-n_b}[V_{fb}^{-1} - V_{rb}^{-1}]$$

$$= \sum_{i=1}^{n} w_i \frac{V_{0i}}{1-n_i}[V_{fi}^{-1} - V_{ri}^{-1}] \qquad (36)$$

where V_{rb} and V_{ri} are the free volumes of blend and pure components at some reference shear rate, respectively.

Since the occupied volume is independent of shear rate, eq. (36) can be expressed in terms of the parameter Θ defined by (9) in the following manner:

$$\Theta_b = \Theta_{rb} + (1 - n_b)\sum_{i=1}^{n} w_i \frac{1}{1-n_i}[\Theta_i - \Theta_{ri}] \qquad (37)$$

where Θ_{rb} is a value of Θ_b at some reference shear rate, and

$$n_b = \sum_{i=1}^{n} w_i n_i \qquad (38)$$

The last equality follows directly from assumption (22), the identity of constants C and K in eqs. (1) and (15), and from the fact that the constant K as a function of shear rate is commonly represented by[7]

$$K = K_0 - (1 - n) \ln \dot{\gamma} \qquad (39)$$

The dependence of the parameter Θ (Θ') on the shear stress τ can be easily derived in a very similar way:

$$\Theta'_b = \Theta'_{rb} + \frac{1 - n_b}{n_b} \sum_{i=1}^{n} w_i \frac{n_i}{1 - n_i} [\Theta'_i - \Theta'_{ri}] \qquad (40)$$

In this case Θ'_{rb} corresponds to a value of Θ'_b at some reference shear stress.

As has been mentioned above, the direct calculations of blend viscosity by means of eq. (24) can be done if the parameter Θ_b is known. This quantity as a function of shear rate or shear stress and temperature can be calculated from eq. (37) using the reference value Θ_{rb}, which should be determined from independent data. There are at least two ways to evaluate Θ_{rb}:

(a) From eq. (16) if the values of parameters A, B, and D in Fulcher–Tamman or Arrhenius equations for blend were determined at some shear rate (shear stress) and temperature, i.e., in reference state.

(b) From the equation

$$\Theta_{rb} = \frac{V_{0b}}{V_{rb} - V_{0b}} \qquad (41)$$

if the specific volume of blend in reference state V_{rb} was measured. The value of V_{0b} can be calculated from (23) using suitable properties of pure components.

Another method making possible the direct calculations of the blend viscosity from experimentally determined specific volume and thermal expansion coefficient was described in our previous paper.[5]

EXPERIMENTAL

Using isotactic polypropylene (iPP), Malen P, and hydrogenated block copolymer isoprene–styrene (EP/S), Shellvis 50, a number of blends of different compositions have been prepared. The obtained iPP–EP/S blends have been investigated to determine their viscosity (as a function of shear rate and temperature) and specific volume (at very low shear rate as a function of temperature). Details of preparations and measurements have been reported in Refs. 5 and 8. In the present work the temperature dependence of viscosity at very low shear rates corresponding to the conditions of the specific volume measurements has been additionally determined.

RESULTS AND DISCUSSION

Equations (15)–(17) suggest that the thermal expansion of different polymeric systems can be directly determined from their rheological behavior if the functional dependence of viscosity on temperature at given shear rate or shear stress is known. Assuming the validity of Fulcher–Tamman or Arrhenius equations for $B = 1^2$ from expressions (15)–(17), it follows that:

—Fulcher–Tamman equation:

$$\frac{\partial \ln V}{\partial T} = \frac{1}{A + T - T_0}. \qquad (42)$$

—Arrhenius equation:

$$\frac{\partial \ln V}{\partial T} = \frac{1}{E/R + T} \qquad (43)$$

The results of our previous and present measurements on rheological and thermal properties of iPP–EP/S blends are summarized in Table I. Table II presents experimental data on similar properties of other polymer systems which were reported in the literature.[9] In all cases the values of the thermal expansion coefficient were calculated at 453 K. The parameters of the Fulcher–Tamman equation for the iPP–EP/S system have not been estimated since the rheological measurements were carried out in the region of high melt temperatures in which the errors connected with the estimation of A and T_0 were very large.

From Tables I and II it can be seen that the values of the thermal expansion coefficients calculated from

Table I Some Properties of iPP–EP/S Blends

Copolymer Content (wt %)	$\kappa_d \times 10^4$ (K^{-1})	$\kappa_A \times 10^4$ (K^{-1})	n 448 K	n 493 K	E_0 (kJ/mol)	$E_{\dot\gamma}$ (kJ/mol) 20 s^{-1}	$E_{\dot\gamma}$ (kJ/mol) 500 s^{-1}	E_τ (kJ/mol) 8 MPa	E_τ (kJ/mol) 12 MPa
0	7.71	2.92	0.402	0.418	24.29	22.33	20.47	47.56	46.06
5	7.15	2.96	0.401	0.415	24.75	22.51	20.52	49.70	47.90
10	6.94	2.87	0.400	0.416	25.21	23.01	20.55	51.11	48.94
15	6.78	2.82	0.402	0.413	25.75	23.30	20.57	51.47	49.46
20	7.57	2.69	0.389	0.410	26.92	24.03	20.57	52.98	50.87
25	7.87	2.71	0.381	0.400	27.14	24.07	20.58	53.54	52.03
50	7.44	2.58	0.330	0.368	28.48	25.11	20.69	60.53	57.44
75	7.16	2.36	0.279	0.325	31.48	27.60	20.94	73.24	67.50
100	6.90	2.03	0.258	0.318	37.17	29.44	21.01	104.76	95.03

expression (43) corresponding to Arrhenius equation (κ_A) are about 3–10 times smaller than those calculated from direct measurements (κ_d), i.e., from the dependence $V = V(T)$. The suitable values of thermal expansion coefficients for different polymers obtained from expression (42) corresponding to the Fulcher–Tamman equation (κ_F) presented in Table II are similar to κ_d. Hence, the Fulcher–Tamman equation is probably more appropriate for description of the temperature effect on thermal properties of polymers.

Table II also presents the values of the parameter Θ calculated from (16) for material constants corresponding to the Arrhenius equation (Θ_A) and the Fulcher–Tamman equation (Θ_F), respectively. For the majority of polymers both values differ by no more than 35%. These differences do not seem to be too large, taking into account that the citied experimental data probably correspond to different types of polymers measured at different conditions. Therefore, in narrow temperature intervals the value of Θ (but not κ!) can be approximately defined as E/RT using the Arrhenius equation.

Experimental data from Table I make it possible to estimate the effect of shear rate or shear stress on specific volume variations according to eq. (18). Assuming that Θ_s corresponds to E_0/RT and Θ to E_{500}/RT, it can be stated that in the temperature interval 448–493 K an increase of relative specific volume V/V_s with increasing shear rate does not exceed 6–7% (for pure EP/S copolymer).

Figure 1 presents the experimental verification of additivity of occupied volume as given by eq. (23) at two extreme temperatures for iPP–EP/S blends. The parameter Θ has been defined as E_0/RT and the activation energy E_0 (Table I) corresponds to the conditions of specific volume measurements, i.e., to low shear rate values. It can be seen that the linearity of occupied volume can be assumed independently of temperature. A temperature rise, however, leads to an increase of occupied volume, which testifies to some small thermal expansion of the occupied volume.

Figure 2 presents the dependence of the material constant C on blend composition at two different shear rates and 448 K for iPP–EP/S system cal-

Table II Comparison of Different Thermal Properties of Polymers Resulting from the Free Volume Theory

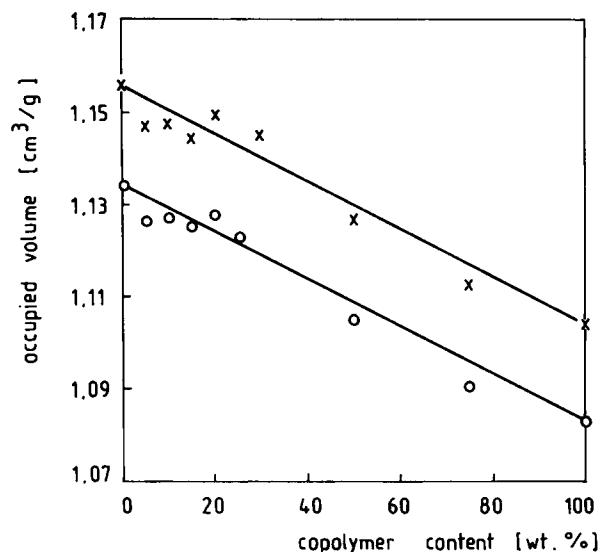| Polymer	$\kappa_d \times 10^4$ (K^{-1})	$\kappa_F \times 10^4$ (K^{-1})	$\kappa_A \times 10^4$ (K^{-1})	Θ_F	Θ_A
Poly(methyl metacrylate)	6.05	3.67	0.56	17.79	28.50
Poly(α-methylstyrene)	5.41	4.59	0.65	27.27	33.19
Polystyrene	5.19	5.19	0.99	14.06	21.24
Polypropylene	5.45	4.89	1.70	7.29	11.95
High density polyethylene	6.08	5.57	2.89	5.02	6.64
Low density polyethylene	7.03	4.93	1.90	7.68	10.62

Figure 1 Effect of composition and temperature on occupied volume of iPP-EP/S blends: (———) theoretical calculations. Experimental data: (O) 448 K; (X) 493 K.

culated from experimental data by means of eq. (24). Experimental points obtained for other temperatures have not been marked since their positions practically do not differ from those corresponding to 448 K. It can be stated that for the iPP–EP/S blends the quantity $C_{\dot\gamma}$ (determined at a constant shear rate) linearly depends on the blend composition according to assumption (22).
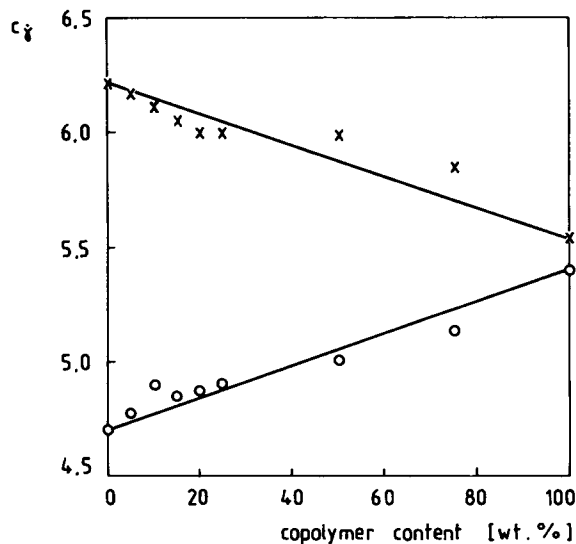
Figure 2 Effect of blend composition on material constant $C_{\dot\gamma}$ at different shear rates: (———) theoretical calculations. Experimental data: (X) 20 s^{-1}; (O) 500 s^{-1}.

Figure 3 presents similar dependence as that in Figure 2 but calculated for two different constant shear stresses and temperature 448 K. It can be seen that in this case a slightly nonlinear course of C_τ with varying blend composition occurs. It is difficult to decide whether this behavior is a general rule for any system or it can be treated as a special case. To clarify this question further, experimental studies of other systems are indispensable.

The effect of shear rate on the parameter Θ for blends of different composition is described by eq. (37). Assuming that Θ can be defined as E/RT, this equation takes the form

$$\frac{1}{1 - n_b} [E_{1b} - E_{2b}]$$

$$= \sum_{i=1}^{n} w_i \frac{1}{1 - n_i} [E_{1i} - E_{2i}] \quad (44)$$

where the subscripts 1 and 2 correspond to values of the activation energy E determined at two different constant shear rates. Similarly, for the shear
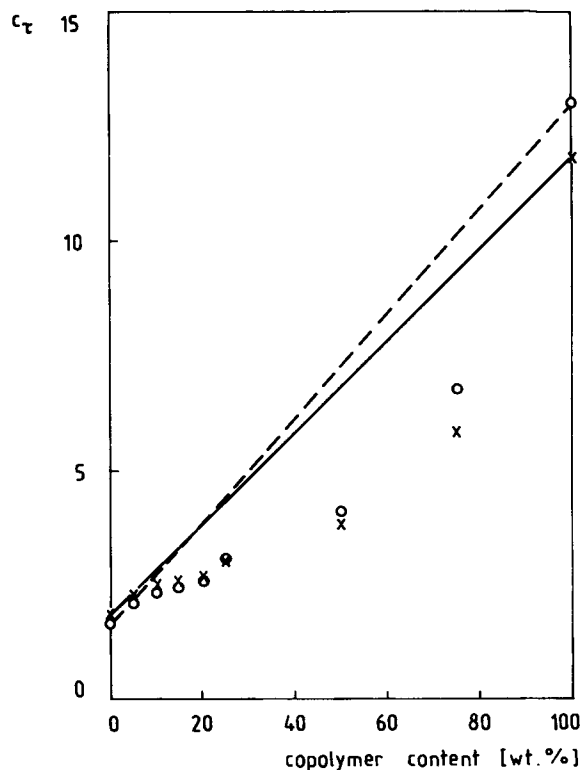

Figure 3 Effect of blend composition on material constant C_τ at different shear stresses. Theoretical calculations: (– – –) 8 MPa; (———) 12 MPa. Experimental data: (O) 8 MPa; (X) 12 MPa.

stress dependence in the strength of equation (40), one obtains

$$\frac{n_b}{1 - n_b} [E'_{1b} - E'_{2b}]$$

$$= \sum_{i=1}^{n} w_i \frac{n_i}{1 - n_i} [E'_{1i} - E'_{2i}] \quad (45)$$

In this case the subscripts 1 and 2 correspond to the activation energy E' determined at different constant shear stresses.

Figure 4 presents the comparison of experimental data with theoretical dependence (44) for the iPP–EP/S system at temperatures 448 and 493 K. The activation energies for blends and pure components have been evaluated at shear rates $\dot\gamma_1 = 20$ s^{-1} and $\dot\gamma_2 = 500$ s^{-1}. It can be seen that the agreement between experimental and theoretical values is satisfactory.

A similar comparison to that in Figure 4 but corresponding to eq. (45) is shown in Figure 5. The suitable activation energies have been determined at $\tau_1 = 8$ MPa and $\tau_2 = 12$ MPa.

In this case considerable deviations of experimental data from the linearity predicted by eq. (45) occur. This behavior was very probable, since the material constant C_τ is also a nonlinear function of composition as has been shown above, and eq. (45) was derived assuming the linearity of C_τ.
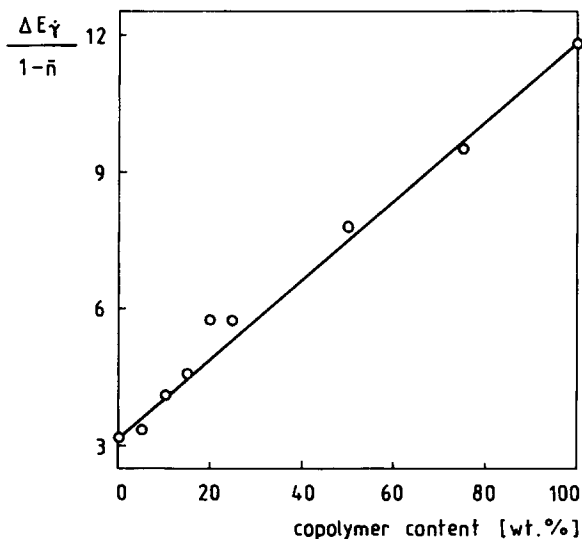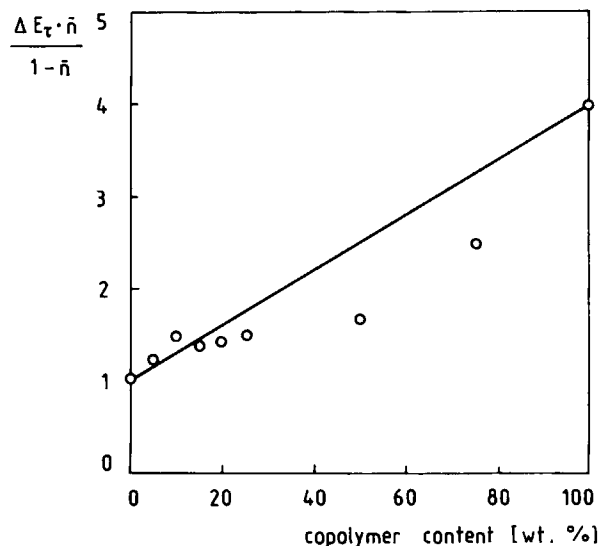

Figure 5   Effect of blend composition on differences between activation energies determined at constant shear stresses $\tau_1 = 8$ MPa and $\tau_2 = 12$ MPa: (——) theoretical calculations; (O) experimental data.

Figure 6 shows the dependence of viscosity of iPP–EP/S blend on its composition for different temperatures and shear rates. Theoretical dependence represented by solid curves was calculated according to eq. (24) with the parameter Θ_b defined as E_b/RT and determined from expressions (37), (38), and (44). Activation energies at $\dot\gamma = 500$ s^{-1} have been used as reference quantities. The broken lines represent the theoretical dependence which was also calculated from eq. (24) but the parameter Θ_b was determined from eqs. (23), (37), (38), and (41).

It can be seen that in the first case (solid line) the agreement between theoretical and experimental data is very good. In the second case, however, distinct deviations of experimental data from theoretical curves occur. This is probably due to the fact that the reference state corresponds to the conditions of specific volume measurements, i.e., to low shear rates. In this region the slope of the flow curve in logarithmic coordinates is not constant but depends on shear rate. Hence, the integration of eq. (34) should lead to a result other than that given by (35) for the constant slope. The last equation has been applied for derivation of expression (37). Moreover, the quantity Θ_{rb} defined by eq. (41) can be determined only indirectly from many independent experimental data. It should be treated as an additional source of errors. For these reasons the method of viscosity calculations based on measurements of the specific volume of a blend in the reference state is probably less effective than that re-
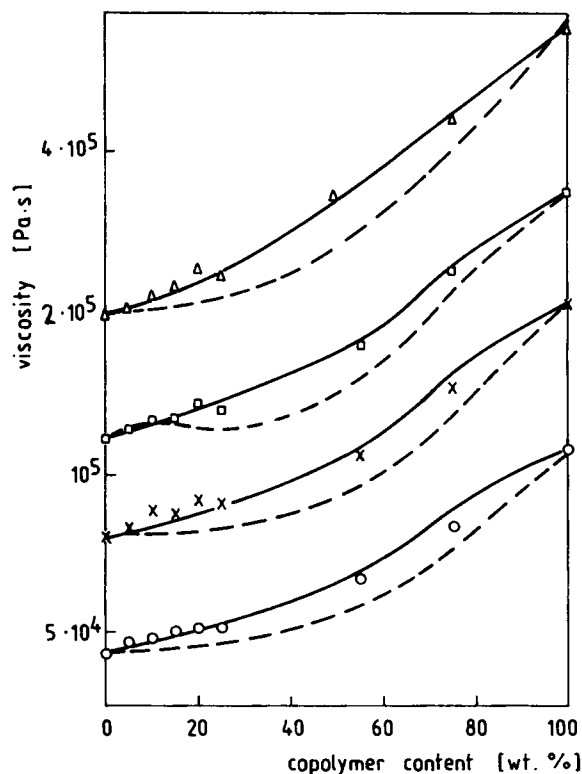

Figure 4   Effect of blend composition on differences between activation energies determined at constant shear rates $\dot\gamma_1 = 20$ s^{-1} and $\dot\gamma_2 = 500$ s^{-1}: (——) theoretical calculations; (O) experimental data.

Figure 6 Effect of blend composition on viscosity of iPP-EP/S blends at different shear rates and temperatures: (——) theoretical calculations based on measurements of activation energy of blend in reference state; (- - -) theoretical calculations based on measurements of specific volume of blend in reference state. Experimental data: ($\triangle$) shear rate 20 s^{-1}, temperature 448 K; ($\square$) shear rate 20 s^{-1}, temperature 493 K; ($\times$) shear rate 100 s^{-1}, temperature 448 K; ($\bigcirc$) shear rate 100 s^{-1}, temperature 493 K.

lying on measurements of activation energy of blend in the reference state. This value practically directly defines the parameter Θ_{rb} and for suitable high shear rates provides the validity of eq. (37).

The blend viscosity at a constant shear stress cannot be quantitatively calculated by any of the methods presented. This is due to the nonlinearity of the material constant C_r discussed above. For these reasons a suitable plot has not been placed.

FINAL REMARKS

Theoretical analysis and its experimental verification show that the free volume theory can be a useful

tool for predictions of many different properties of polymers and polymer blends. Experimental data obtained for iPP-EP/S blends testifies to the validity of all assumptions presented above if the blend viscosities are compared at a constant shear rate. In the case of a constant shear stress, one of the most important assumptions, i.e., the additivity of material constant C for blends in the Doolittle equation is not satisfied, and therefore the agreement between experimental and theoretical data is poor. It is not quite clear, however, whether this assumption effecting the analytical form of many expressions derived in this paper is generally applicable for any polymer blend at a constant shear rate and not applicable at a constant shear stress. Hence, it should be experimentally proved for other polymer systems. From the above considerations it follows that a need for the use of another analytical expression adequately describing C as a function of composition and properties of blend components would lead to quite different equations for activation energy of blend, blend viscosity, etc. This fact should be taken into account if the proposed method is applied for description of rheological and thermal properties of any system.

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